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(54) Title:

A Procedure and an Apparatus for the Protective Coating of Electrically Conducting Objects by means of Plasma

The invention concerns a procedure and an apparatus for protective coating of electrically conducting objects by means of ionized vapors from a plasma engendered by a glow discharge, whereby the feed of electrical energy into plasma is effected by periodically repeated pulses. In this way, the achievement is gained, that the parts to be coated are subjected to an ion impingement, that is to say, a temperature exposure, which is capable of being incrementally measured and controlled over a wide range. By the superimposition of pulsed and non-pulsed magnetic fields, the coating can be additionally influenced.

Procedure and Apparatus for Protective Coating of Electrically Conducting Objects by Plasma

CLAIMS

Claimed is:

1. A procedure for the protective coating of electrically conducting objects by the Physical Vapor Deposition method by means of ionized vapors engendered by direct current plasma of a glow discharge, therein characterized, in that the feed of electrical energy is carried out by the use of periodically repeated direct current pulses.

2. A procedure in accord with claim 1, therein characterized, in that pulses are employed with a potential of more than 100 V, especially between 200 and 800 V.

3. A procedure in accord with the claims 1 or 2, therein characterized, in that the pulse current at the workpiece is applied with a density of 0.1 mA/cm^2 up to 1 A/cm^2, especially at 0.5 mA/cm^2.

4. A procedure in accord with the foregoing claims, therein characterized, in that pulses are applied with an energy concentration of 1 to 900 W/cm^2, in particular, 30 W/cm^2.

5. A procedure in accord with the foregoing claims, therein characterized, in that the duration of a pulse lies between 10 and 1000 μs, especially 30 to 200 μs.

6. A procedure in accord with the foregoing claims, therein characterized, in that for the energy free time-interval between successive pulses, between 10 and 1000 μs, especially 30 to 200 μs are used.

7. A procedure in accord with the foregoing claims, therein characterized, in that for the average plasma energy density, a value between 50 mW/cm^2 and 5W/cm^2 is used.

8. A procedure in accord with the foregoing claims, therein characterized, in that coating is carried out in the case of pressures of less than 100 Pa, especially at 0.1 to 1 Pa.

9. A procedure in accord with the foregoing claims, therein characterized, in that an external magnetic field is imposed upon the plasma.

10. A procedure in accord with claim 9, therein characterized, in that a pulsating magnetic field is employed.

11. A procedure in accord with the foregoing claims, therein characterized, in that the current pulses for the establishment of plasma and a magnetic field are synchronized.

12. A procedure in accord with the foregoing claims, therein characterized, in that the magnetic field direction is synchronously reversed.

13. A procedure in accord with the foregoing claims, therein characterized, in that external heat is radiated into the plasma.

14. A procedure in accord with the foregoing claims, therein characterized, in that the coating procedure is controlled by a microprocessor.

15. A procedure in accord with the foregoing claims, therein characterized, in that an arc discharge in the plasma is automatically recognized and within a less than 10 μs the pulse shuts itself off.

16. An apparatus for the carrying out of the procedure in accord with one or more of the claims 1 to 15, wherein said apparatus incorporates a vacuum chamber, in which are placed; the workpiece to be coated, a vaporization source, as well as an anode and cathode for generation of a glow discharge in the plasma, having further connections to a source of electrical energy, therein characterized, in that the source of energy is a pulsed current source.

17. An apparatus in accord with claim 16, therein characterized, in that the pulsed current source possesses a controlling power release, especially comprised of transistors, with an output potential of more than 100 V, especially 200 to 800 V, and a switching time of less than 5 μs.

18. An apparatus in accord with the claims 16 and 17, therein characterized, in that the source of current possesses a control with an arc sensing switch.

19. An apparatus in accord with claim 18, therein characterized, in that the arc sensing switch has an active connection with the source of current.

20. An apparatus in accord with claim 16, therein characterized, in that the said apparatus possesses a magnetron, especially a planar magnetron with capabilities for pulsed current.

21. An apparatus in accord with the claims 16 to 20, therein characterized, in that the walls of the vacuum chamber are designed to be heated.

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Procedure and Apparatus for the Protective Coating of Electrically Conducting Objects by Plasma

Description

The invention concerns a procedure for a protective coating by means of plasma and an apparatus for carrying out of the said procedure.

For the coating of objects, procedures are known, wherein the material of the coating separates out of a vapor phase to collect upon the workpiece. In order to minimize the effects of temperature stress created by the condensation of the vapors upon surfaces of the workpiece, wherein the heat of condensation become freely released heat, the practice has been to execute the vaporization of the coating material in a vacuum. The procedures, commonly known under the acronym, "PVD" (Physical Vapor Deposition), for the coating of workpieces differentiate themselves by the differences in the various manners in which the respective vapors must be generated. The properties of the coatings essentially better themselves when the coating itself is done within a plasma atmosphere. The ionized vapor can be accelerated in its collection or precipitation on the workpiece by means of the application of external magnetic or electrical fields. Thereby the vapor instigated deposition rate can be advantageously increased.

The equipment used for plasma depositions engender undesirable, high temperature effects on workpieces and the coating materials. This is due to the high kinetic energy of the precipitating particles. This high energy also leads to the fact, that the said particulate, under these conditions, forms a coating which itself is easily removed from its substrate. These disadvantages can go so far as to bring about a procedure described in DE-PS-22 03 80, wherein it was taught that the deposited layer would grow only, until the removal rate equaled the deposition rate, and on this account, coatings of equal thickness could be made independently of the length of the deposition procedure.

In the majority of applications, one would like to achieve the highest possible growth of the deposited layer. The consequence is, however, that the removal rate, because of colliding particles and an unequal thermal burden, functions at a disadvantage. The unfavorable changes in the surface of the workpiece, because of precipitating ions consist of a roughing of the surface or a penetration therein and leaving evidence of both faults as well as the effects of temporary electrical charges on the workpiece surface.

The high number of impacts from particulate, of the general magnitude of a piece number of 10^{17} /cm^2 each second leads to a high probability for chemical reactions. In many cases, consideration has to be given to a substantial incorporation of foreign material, that is external substances in

the produced coatings. Beyond this, severe temperature changes in the workpiece as well as in the coating must occur because of the high kinetic energy of the impacting particulate.

The plasmas employed in known equipment are predominately generated by electrical discharges. The physical points of this said discharge consist of two current carrying electrodes set within the plasma Between these electrodes, upon the ignition of the discharge, the evaporated, gas formed material is emitted. The flow of current is assured by the plasma, and simultaneously, the applied electrical energy for the upholding of the plasma condition, subjects the oven and the workpiece to a high temperature loading. The oven walls, as well as the workpiece to be coated, must now be cooled.. In a case of coating different objects, it is possible, that those objects with a greater ratio of outer surface to volume can be easily overheated. The result brings about a disappointingly high reject quota along with a higher cost for the operation, since only similar workpieces can be handled in one batch. The temperature difference between the inner oven temperature and a cooled oven wall, which is necessary for the removal of the excessive heat, leads to varying, localized rates of deposition in the oven. The result includes coatings of different qualities.

The purpose of the invention is to make available a procedure, wherein the disadvantages of the current procedure are avoided, and in place of the former methods, to make known, by means of coating with ionized vapors, features of lesser operational costs, lower reject quotas, higher quality and improved procedure conditions.

This purpose is achieved, in that a feed of electrical energy into a plasma by means of periodic, repeated pulsing is put into action. This method of operation permits an advantageous protective coating onto objects, because, in accord with the invention, only surprisingly lower temperatures are applied. At the same time, the operational costs advantageously reduce themselves and reject quota drops.

In one embodiment of the invention, provision has been made, that the pulse should show a voltage of more than 100 V, especially this should lie between 200 V and 800 V. The pulses enable a plasma to remain alive within the vacuum chamber, which, first, considerably reduces the dangers of the formation of arcs and second, contributes to an effective coating of workpiece objects. With the aid of pulses of this type, it becomes possible to even coat surfaces of object structures, which possess a ratio greater than one, that is, relative to length/diameter, as measured by borings.

Another embodiment of the invention proposes, that the said pulse incorporate a current, which induces in the workpiece a current density between 0.1 mA/cm^2 of the workpiece surface area up to 1 A/cm^2, especially 0.5 mA/cm^2. Current densities of this magnitude lead to excellent growth rates of the deposited layers accompanied by an essentially low consumption of electrical energy.

In yet another embodiment of the invention, the provision is, that the pulse possesses an energy, the density of which, during the life of the said pulse, lies between 1 W/cm^2 and 900 W/cm^2, in particular, 30 W/cm^2. Because of the advantageously wide period, during which the energy density is active, it is possible that objects of very different geometries can be coated.

In a further embodiment of the invention, provision is made, that the pulse has a life

between 10 μs to 1000 μs, preferably at 30 μs to 200 μs during which no energy feed is actuated. In practical and interesting applications, such intervals have functioned well. Further, with this arrangement, lesser areas permit advantageous operation in an especially reliable and economic manner.

In yet another advantageous embodiment of the invention, provision has been made, that an average energy density of the plasma can be easily chosen between 50 W/cm^2 to 5 W cm^2. This procedure allows itself to adapt to very differently designed objects, whereby a disadvantageous overheating of the object or individual components thereof can be predominately avoided.

In another embodiment of the invention, the proposal is, that the coating be applied under a pressure of less than 100 Pa, advantageously between 0.1 Pa to 1 Pa. The procedure allows itself to be run under unusually high pressures, so that no especially severe conditions need be placed on the vacuum chamber. Particularly effective growth conditions for coatings, however, preferably are achieved at given lower pressures.

In yet another advantageous embodiment of the invention, provision has been made, that the plasma be subjected to a superimposed magnetic field, this being done by a magnetic field built up pulsewise. In this case, an additional increase in the growth rate of the deposition is achieved. The pulsing of the magnetic field leads to an advantageous lessening of the consumption of energy.

In another embodiment of the invention, provision has been made to bring about a synchronization between first, the current pulse of the plasma and second, the current pulse for the buildup of the magnetic field, especially with the knowledge that the magnetic field is capable of synchronously reversing its direction. This formulation advantageously disperses the vapor atoms, whereby even object shapes which are especially difficult to coat can be successfully treated.

In a further embodiment of the invention, the proposal is, that a radiation of external heat be made into the plasma. The oven temperature to support chemical reactions or for the aid of diffusion procedures can be set especially exactly at specified levels and can be reliably held at that point.

In a further embodiment of the invention, provision has been made, that the pulse be a direct current pulse. Thereby, the plasma can be especially well monitored and material transport influenced in a wide range.

In an additional embodiment of the invention, the provision is, that an automatic control of the procedure be carried out by a microprocessor. Those parameters for procedure guides seen as optimal for a specific batch can be advantageously reproduced with the aid of the storage of the said microprocessor and then called up again in a case of similar batches for an automatically controlled procedure.

In a further embodiment of the invention, the provision is that the procedure, in the case of PVD procedures, especially when ion deposition is employed, be carried out by arc vaporization or by sputtering equipment. In the case of procedures of this kind, which previously were burdened by a high thermal loading of the object to be coated, these can be very well adapted to the invented procedure, since the invented coating procedure is protective of the object.

In a further embodiment of the invention, it is proposed, that an automatic sensing of an arc discharge in the plasma be activated, whereby a self actuating shutting off of the pulses takes place in a time interval of less than 10 μs. In this case, even the unexpected occurrence of an arc discharge, as far as the invention is concerned, does not lead to a disadvantageous impairment of a previously deposited coating. Before the action of an arc can build up, the energy feed is advantageously shut off.

For the execution of the procedure, an apparatus is provided, which is comprised of a vacuum chamber, in which a workpiece to be coated, a source of vapor, an anode, a cathode for the generation of a glow discharge, and finally a electrical source of energy are to be found. This apparatus description would apply to a form of an ion coating or a sputter device, whereby, in accord with the invention, provision has been made, that the energy source is designed as a pulsating current source. Thereby, the energy consumption of the entire equipment is essentially lessened and the previously necessary cooling systems can be laid out to be smaller, or indeed, eliminated entirely.

In a further embodiment of the invention, provision is made, that the pulsating current source possesses a power limiting device, which consists especially of transistors. This power limiting device would be designed for an output voltage of more the 100 V, preferably 200 V to 800 V, and would react in a switching time of less than 5 μs. The transistors offer especially advantageous switching times at high potentials, so that, advantageously, favorable pulse shaping can be achieved, which would nearly approach, for example, a square cornered shape and permit a precise guidance of the procedure.

In a further embodiment of the invention, the provision allows that the current source possesses a control with an arc sensor switch, wherein said arc sensor switch has an active connection to the source of current, in order that this can be shut off upon an occurrence of arc discharges. Thereby, the operation of the apparatus is made more reliable and the reject quota brought into a more favorable ratio.

In a further embodiment of the invention, the provision is that the equipment possess a magnetron, especially a planar magnetron, which in turn is equipped with a pulsed current supply. In this way, a rapid growth of a substantial layer thickness becomes possible, accompanied by a relatively small consumption of power.

In a further embodiment of the invention, the provision is, that the wall of the vacuum chamber be heatable. Thereby, growth conditions can be exactly and uniformly controlled. Also objects with differently designed ratios for surface / volume can be treated in the same lot.

The invention is hereinafter described in drawings, from which advantageous details may be inferred. The drawings show in detail, in:

Figs. 1 to 3	applications of the invented procedure, demonstrating various coating procedures,
Fig. 2	a case of ion plating,
Fig. 3	a illustration of arc vaporization,

Fig. 4 a voltage-current density characteristic curve of a discharge,

Fig. 5 a power characteristic curve of a plasma, and

Fig. 6 a comparison of workpiece characteristics between a known and an invented procedure.

Fig. 1 shows, schematically, a coating apparatus which operates in accord with the principle of atomization or, more commonly, the known "sputtering". The coating procedure is carried out in a vacuum chamber 1, which, by means of a fitting 2, is connected to a vacuum pump. Upon the sputtering procedure, the surface of a target 3, this consisting of coating material, is connected in the circuit as a cathode and receives the impacts of high energy ions. The energy density attains a value of approximately 3 W/cm^2 and the gas pressure at this location reads a few Pa. A gas, which is to form the said plasma, is admitted into the vacuum chamber 1 through a connection fitting 6. Reference number 4 designates a shield behind the target 3. The potential, established by the source 9 of invented pulse voltage and applied between the opposed terminals 7 and 8 serves the purpose of accelerating ions in their travel toward the target 3. It is from the impact of ions against the surface of the target 3 whereby coating material is displaced from the surface thereof.

Fig. 2 demonstrates the installation of an invented pulsed voltage source 9 during ion coating. Equipment parts which are functionally the same are given the same reference numbers as in Fig. 1. In the case of the ion coating, the workpiece 5 now serves as a cathode. Behind this is again located a shield 4. The vacuum chamber 1, which can be evacuated through a vacuum pump access fitting 2, can then be filled with gas through an inlet connection piece 6. In addition to this, a vaporization source 11 is bound to the anode 10. Between the anode 10 and the workpiece 5 is generated a glow discharge plasma 12, which is maintained by the invented pulse voltage source 9. The vaporization is done with the aid of the said vaporization source 11 in the presence of the glow discharge plasma 12,

On this account, from the now cathode-workpiece, upon the progress of the coating and by means of the high energy ions, the already established coating is once again being partially atomized away at a lesser rate than that of its deposition. The workpiece finds itself at a distance of some 20 to 50 cm from the said vaporization source. On the workpiece carrier lies a negative high voltage potential of 100 V to 1000 V. The current density runs about 0.5 mA/cm2. The gas pressure of a few Pa activates a turbulence of vapor atoms, so that optionally shaped objects can be coated.

A variant of the ion coating procedure is shown in Fig. 3, wherein the vaporization is carried out by means of an arc. For this arrangement, in Fig. 3, within the vacuum chamber 1 vaporization sources 13 are arranged, which normally are in a circuit as cathodes. The electrical arcs, which scan over the surface of the vaporization source have a current density of 60 A to 400 A at about 20 V. At the base points of the arcs, localized overheating is found and therewith a corresponding vaporization of coating material.

A large portion of the vapor, some 90%, is ionized and has a high initial energy of about 10 eV. This ionized portion is to be additionally accelerated by means of the cathode workpiece 5, which has already been subjected to a negative prevoltage. The coating is normally applied with a pressure of a few Pa. Even in this case, the acceleration of the ions can be influenced in great part by the pulsed potential source 9.

Advantageous in the case of sputtering is increasing the plasma density beyond the source with the aid of a magnetic field. This is produced by the so-called magnetron, that is, a planar magnetron. This high plasma density is achieved by means of a special arrangement of an electrical and a magnetic field of high power above the workpiece carrier. The magnetic field forms, under these circumstances, a closed, semi-torus shaped loop, this being an electron source since the field lines run in and out of the target surface. Externally to this loop, electrons are accelerated on cycloidal tracks, whereby their effective ionization paths are essentially lengthened. The space, in which ionization takes place, is proximal to the target and in this way accentuates the high plasma density. As a result of the negative prevoltage application to the target, ions are accelerated from the plasma to strike the workpiece, atomizing the surface thereof. Even in this case, the pulsed addition of energy in the electrical and magnetic field eases the control of the coating procedure and increases the vaporization rate.

A common element to all the procedures described in the Figs. 1 to 3, is that universally a glow discharge occurs. The characteristic curve of such a glow discharge is presented in Fig. 4. The abscissa 14, characterized thereby the current density and the ordinate 15, represents the voltage. The graph curve 16 separates itself into 7 clearly different zones, which successively are designated by the numbers 17-23. The procedure makes use, in this arrangement, of the zone designated 21, which is the recognized area of he anomalous glow discharge, which differentiates itself by means of higher current density and higher voltage from any one of those within the flat run, designated as zone 20 of the normal glow discharge. The usual arcing occurs in the zone 23. Because of the high voltages present in zone 21, as well as high current densities, the energy flow of the plasma is especially intensive.

Due to the current flow existing in the plasma state, the positive ions migrate to the negative cathode and the electrons move in the opposite direction. The current flow through the plasma exerts a very strong effect on the workpiece. Since, for the upholding of the plasma, a minimum voltage is required, the ions undergo an acceleration, which, in the case of known procedures, leads to a partial eradication of the already deposited layer.

Fig. 5 shows, on the other hand, the power characteristic of a plasma in accord with the present invention, which enables the deposition of an essentially greater layer of protective coating on the workpiece. Surprisingly, the invented power characteristic properly maintains the physical conditions for the anomalous glow discharge in the oven atmosphere. The temperature effects upon the substrate during the coating is held surprisingly minimal, that is to say, they may be held within closely controllable limits.

An advantageously, uniform temperature forms in the reaction space. The occurrence of light emitting arcs, moreover, is essentially lessened by the invented procedure.

Since only a very narrow band width within the limits of the anomalous glow discharge can be of value, and which width reduces itself in a case of higher pressures inside the vacuum chamber, this brings about special difficulties for the coating of different workpieces combined in a single batch. The danger is apt to arise, wherein smaller pieces with a large surface/volume ratio can be easily overheated. Otherwise, the energy flow through the plasma cannot be optionally adjusted to a lower level, because if that were done, the plasma state would collapse.

In accord with the invention, power is introduced into the plasma in pulses from a pulse-voltage source. In Fig. 5 an individual voltage pulse 24 possesses a peak voltage 25, which meets the requirements for the anomalous glow discharge in zone 21 of Fig. 4. Normally, the interval 26 of the voltage pulses 24 is approximately 10 µs. Additionally in Fig. 5 the abscissa 27 is a time axis, while the ordinate 28 depicts power. The power of the individual impulse 24 can vary between a minimal value p_{min} and a maximum value p_{max}. These power values correspond to the two endpoints of the zone 21 of the anomalous glow discharge of Fig. 4. The height of the power pulse 25 corresponds to the required power of the plasma, namely p_{pla}. The high p_{temp} represents the required power for the maintenance of the temperature in the reaction space. This energy input, represented by the surface 29, corresponds to the entire surface of an individual pulse 24. Compared to a direct current supply of voltage, the surface 29 represents an essentially lesser energy. By means of a variation of the pauses between the impulses, it is possible that the energy input would be changed in surprisingly large areas. The minimal energy input serves not for the purpose of maintaining the plasma, but rather for the support of a uniform temperature. In order to achieve a uniform temperature within the equipment, it is necessary that the energy input p_{temp} be at least high enough to match the heat loss of the equipment.

Fig. 5 shows, as an ideal pulse shape, a right-angled pulse whereby the supply loading, in as short a time as possible, rises from zero to the required value and likewise falls in the same manner. The duration of the pulse is selected at less than 100 µs. Surprisingly, within this short duration, the formation of arcs very seldom occurs. The duration of the pauses between two pulses is selected to be so short, that typically, it is less than a few 100 µs. In spite of this, the glow discharge ignites itself easily at the next impulse.

The ratio between the duration of the pulse to the duration of the pause can be widely changed in the equipment, so that it is possible to almost completely dispense with a cooling of the chamber walls, and even undertake separate heating of the same. This action would result in a noticable better temperature dispensation within the batch.

Fig. 6 depicts schematically in the upper half, left of the center line, an oven with cold walls 30 and oppositely, to the right thereof, is shown an insulated oven, but with heated walls 31. On the workpiece carrier 5 are different workpieces 32 to be coated, which are vertically placed. The oven walls, in accord with this, form different temperature profiles. The graph of the temperature profile, with the said heated walls, is designated as 33, and that with cold walls is shown as 34. The ordinate therewith is graduated in temperature values. Fig. 6 thus shows therewith the temperature distribution within the oven by means of

the location fixed by the abscissa. Clearly, the essentially more uniform temperature profile 33 can be recognized, wherein the temperature drops only within the insulation from the inner oven temperature to the outside ambient temperature.

The procedure in accord with the invention, characterizes itself, on this account, by means of an essentially reduced reject rate. It allows itself, moreover, to be controlled within wide areas, so that it finds automatization to be acceptable. Beyond this, operational costs are less. In spite of these advantages, higher coating rates are enabled, since the deterioration of the substrate by means of ion impacting is reduced and on this account, fewer particles are scoured from the substrate, that is, from the already deposited coating.

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